

Title: Purification of off-gases from gas-fired plants

The invention relates to a method and apparatus for purifying off-gases from gas-fired plants and specifically gas engines.

Gas engines are used *inter alia* for combined heat and power (CHP) generation and for this reason are used to an increasing extent because in
5 this way energy savings, and hence a reduction of CO₂ emissions, can be accomplished. However, a drawback is that small-scale energy generation with CHP gas engines leads to increased emissions of NO_x and methane compared with large-scale electricity generation in power stations.

In recent research, the methane problems have been mapped and the
10 methane slip is estimated to be 1.8% of the primary fuel deployment (see: Gastec, 2001: Kwaliteit gasmotoren in Nederland [Gas engine quality in the Netherlands], Gastec report GL/010476, Gastec, Apeldoorn). Methane is a greenhouse gas which, on a weight basis, is 21 times stronger than CO₂ (100 years of integration time, including indirect effects). However, methane slip
15 not only means a contribution to the greenhouse effect, so that the favorable effect of CHP on CO₂ emissions is partly undone again; methane slip also means a reduction of the efficiency of the plant. For all sources of non-CO₂ greenhouse gases, it is currently being investigated what the possibilities are for emission reduction.

20 The NO_x emission of a gas engine is considerably higher than that of large-scale energy generation. As a result of increased CHP in the Netherlands, the reduction of acidifying emissions in the Netherlands has slowed down. According to the expectations of the Energy Research Center of the Netherlands (ECN), the CHP engine fleet will grow in the next 10
25 years, and with unchanged regulations NO_x emissions will increase proportionally. For Europe a similar growth is expected (see: ECN, 2000: "Mogelijke effecten van NO_x-beleid op het warmte-krachtpotentieel"

[Possible effects of NO_x policy on the heat-power potential"], ECN report ECN-C--00-111).

Controlling simultaneous NO_x and methane emissions by taking engine measures as a rule presents problems in gas engines, since there is a trade-off between methane and NO_x emissions and also between energy consumption (CO₂ emission) and NO_x emission: engine settings that are favorable in respect of NO_x are often unfavorable in respect of methane emission and the energy consumption.

There are a number of possibilities for emission reduction of the individual components, NO_x and methane. For NO_x emission reduction, engine measures can be taken, but the reduction potential of NO_x is limited to about 50% and these measures often result in an increase of the methane emission and a rise of the energy consumption. Another measure for NO_x emission reduction is selective catalytic reduction (SCR) of NO_x using ammonia or urea. However, on the scale of a gas engine, this is a relatively expensive measure, which moreover requires additional deployment of energy-rich co-reagents. For methane emission reduction there is no proven technology yet, not least because emission requirements for methane are currently still lacking. However, there are a number of possibilities. Engine measures can reduce emissions, but often result in an increase of the NO_x emission. Further, methane in the waste gases may be catalytically oxidized, though with limited conversion efficiencies.

Methane-deNO_x is proposed as a measure for emission reduction of both components in the case of lean-burn gas engines; however, the measure is not yet available on a realistic or pilot scale, while on a lab scale, efficiencies of NO_x emission reduction remain limited under the more realistic conditions to 50% at a maximum (see for instance: Tena E. *et al.*, "Cogeneration and SCR of NO_x by natural gas: advances towards commercialisation", NOXCONF 2001, Paris). According to the literature, SCR of NO_x with methane does not proceed, or proceeds very slowly, so that

very high contact times (corresponding to very low gas velocities, for instance expressed in gas hourly space velocity, GHSV) are needed to come to an acceptable NO_x conversion. According to the literature, such low GHSV values render practical application impossible. Moreover, the catalytic conversion of NO_x with CH₄ does not proceed selectively. This limitation in selectivity is caused by the chemical stability of methane, which only becomes reactive at elevated temperature. At this elevated temperature, the catalytic reaction of CH₄ with NO_x is not selective anymore with respect to the non-catalytic reaction with combustion air.

Another technology for DeNox is the selective catalytic reduction of NO_x with hydrocarbons, in particular higher hydrocarbons. It proceeds especially efficiently and selectively when olefins (such as propene) are used as reductant. In the use of aliphatics (propane, butane), the reaction proceeds less successfully.

A possibility for simultaneous emission reduction of NO_x and CH₄ involves the switch to stoichiometric combustion in a gas engine. Given such a stoichiometric combustion, a three-way catalyst can be used for the simultaneous removal of NO_x, CO and higher hydrocarbons. A stoichiometric combustion entails a few drawbacks where the heavier-duty engines or engines with a high specific load are concerned, such as a lowered energetic efficiency and an increased thermal loading.

In virtually every petrol-powered passenger car driving around at the moment, a stoichiometric combustion with three-way catalyst is used successfully. However, because methane in the exhaust gases of a gas engine is much less reactive than the higher hydrocarbons from an engine running, for instance, on petrol, the efficiency of a three-way catalyst in the emission reduction of specifically CH₄ remains limited when CNG is used as fuel.

US-B1-6 357 223 discloses a method for converting compounds that can poison catalysts in off-gas streams. To this end, these compounds are

reacted with particular active compounds, which are formed from water vapor or other gases, utilizing e.g. UV light or corona discharge. In this method, *inter alia* NO₂ may be formed, which is not desired.

The object of the present invention is to provide a solution to at least
5 a part of the above-mentioned problems and is specifically directed to purification of off-gases from gas-fired plants. The crux of the problem is that methane, compared with other hydrocarbons, is insufficiently reactive. By making use of a plasma, methane is converted into more reactive components, which are better able to perform the desired catalytic reactions.
10 It has been found that off-gas streams of gas-fired plants can be very suitably treated in a step in which so-called plasma assisted catalytic methane conversion is carried out. According to the invention, the methane can be converted with the aid of oxygen (for instance coming from the air; "plasma-assisted oxy-cat"), so that a decrease in the methane content is
15 obtained. Also, the methane can be converted with NO_x present in the off-gas ("plasma assisted methane-DeNO_x"), whereby a reduction of both NO_x and methane can be achieved in that NO_x is reduced by the methane present. Accordingly, the invention concerns a method for reducing methane contents, and possibly NO_x contents, in an off-gas stream of a gas engine,
20 wherein the off-gas stream is contacted with a plasma and a catalyst. According to the invention, the whole off-gas stream, or at least a substantial part thereof, is subjected to *in situ* plasma treatment, in contrast to the method of US-B1-6 357 223, where only a fraction of the off-gas stream is passed through a corona discharge reactor, a so-called
25 remote corona application.

Moreover, according to the invention, each part of the off-gas is contacted with radicals which are generated, spatially well distributed, in the plasma reactor. Because of short radical recombination times (order of magnitude is typically 1 to 100 microseconds), the radicals produced in a

remote corona discharge will be less effective for the intended chemical conversion of NO_x.

Thus, an emission reduction of CH₄ and if desired NO_x is obtained, moreover with possibilities of increasing the total efficiency (sum of energetic and thermal efficiency) of the gas-fired plant. According to the invention, it is for instance possible, in a gas engine, to raise the compression ratio, to advance ignition, or to set the air/fuel ratio such that a lower fuel consumption is realized and the energy demand of the plasma is compensated. This setting yields a lower hydrocarbon emission and the increase of the NO_x is undone by the plasma assisted catalytic reduction of NO_x.

Fig. 1 schematically shows two embodiments according to the invention. In the embodiment according to Fig. 1A, the off-gas of a gas engine is first passed through a plasma reactor and subsequently through the catalyst bed. In the embodiment schematically represented in Fig. 1B, the plasma reactor and the catalyst bed are integrated.

The invention is specifically effective because the exhaust gas in most cases contains sufficient methane to reduce NO_x completely. Should this not be the case, the methane content in the exhaust gas can be increased relatively simply through a different setting of the plant.

Although it cannot be stated with certainty what the most active components are that play a role in the chemistry of the present invention, it is assumed – without wishing to be bound to any theory – that according to the invention the following reactions occur.

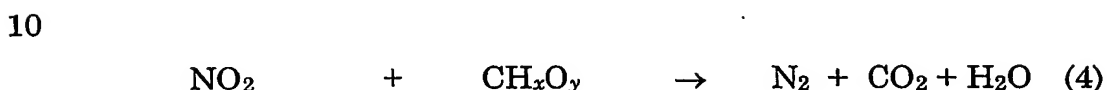
In the plasma, there are free electrons with a characteristic electron energy in the range of 1-10 eV. The free electrons generate a large variety of chemically reactive particles in the exhaust gas, such as radicals (OH) and ions (CH₃⁺). CH₄ is converted both in a direct manner by electrons and in an indirect manner by radicals and ions. An occurring direct reaction is dissociative coupling of electrons with CH₄:



In addition, in the plasma reactor, nitrogen monoxide (NO) is
5 converted according to:



The reduction takes place on the catalyst:



Although a plasma reactor is capable of activating gas molecules, the
reduction of NO_x to N₂ cannot be effectively accomplished with it. Similarly,
15 known catalysts for catalytic conversion of NO_x with the aid of
hydrocarbons under realistic conditions are not suitable for the conversion
of methane and NO_x to water, CO₂ and nitrogen. Surprisingly, with the
combination according to the invention, it has been found that an effective
reduction of NO_x with methane can be achieved.

20 For catalytic conversion of NO_x with methane, it is important that
direct conversion of methane to CO₂ proceeds in a controlled manner,
because CO₂ is not reactive anymore in the catalytic conversion of NO_x;
however, complete conversion of CH₄, either in reaction with NO_x or in
reaction with O₂ from combustion air remains desired. According to the
25 invention, the controlled conversion of CH₄ is accomplished by use of the
plasma. Again without wishing to be bound to any theory, it is assumed that
the first oxidation step of CH₄ in the presence of plasma is no longer
velocity-determinative (whereas this step is velocity-determinative in
"conventional" oxidation of CH₄, that is, oxidation – combustion – without

use of a plasma, because this first oxidation of CH_4 then has the highest activation energy). Through use of the plasma, the forming reactions of all oxidation products from methane (CH_3OH , CH_2O , CO , H_2) have a more or less equal, low, activation energy and these components will be formed in a more selective manner.

According to the invention, the plasma is generated by ionization of the components in the gases by means of a high electrical or electromagnetic field (for instance generated by microwaves). A suitable plasma reactor provides discharges at relatively high electrical fields (as a rule *ca.* 1-100 kV/cm, typically 10 kV/cm). As a result, free electrons, reactive radicals, ions and partially oxygenated compounds (CH_xO_y) are formed in the gaseous phase. The relatively high electrical fields are necessary because the pressure is also relatively high, viz. approximately atmospheric (this is high compared with customary plasma applications). Preferably, an AC voltage is used, which preferably has a frequency of 10 Hz to 100 kHz, typically *ca.* 1 kHz. Preferably, the electrical field is generated between a pair of electrodes, at least one of the electrodes being fully insulated from the off-gas by an electrically insulating layer consisting of, for instance, glass or ceramic. Because of the homogeneous spatial distribution of plasma filaments, which enable an effective *in situ* treatment of the complete gas stream, the power density (W/cm^3) of the plasma can remain limited. The power density of the plasma is determined to a large extent by the frequency of the plasma. This frequency is preferably below 1 kHz.

Preferably, the plasma is maintained with the aid of a partial discharge. Preferably, the partial discharge is generated by the use of a dielectric, such as ceramic or glass, which, preferably completely, covers one or more of the electrodes in the plasma reactor. In this way, a more compact apparatus can be obtained.

The temperature for performing the plasma reactions and the catalytic reactions are preferably set at 300 - 500 °C, but this may vary for

different applications. For use in the automobile industry, a temperature of approximately 350 °C is optimal. For combined heat and power systems, this temperature may be higher, for instance 360 - 370 °C.

As catalyst, in principle all known three-way catalysts, hydrocarbon-
 5 NO_x-SCR catalysts or oxidation catalysts are suitable, in particular
 catalysts based on zeolites (which may or may not be ion exchanged) or
 metal oxides such as γ- alumina, if desired activated with metals as silver,
 indium, platinum, palladium, copper or rhodium. In the choice of a suitable
 catalyst system, the following considerations can play a role. Suitable
 10 catalysts for use in CH₄-deNO_x or methane oxidation must meet a number
 of requirements in respect of activity, stability and selectivity.

The catalysts should be active in a relatively wide temperature range
 of preferably about 200 °C to about 400 °C. It is requisite that sufficient
 conversion be obtained at high GHSV, typically greater than 50 000 h⁻¹,
 15 running up to approximately 150 000 h⁻¹ or more. The catalyst systems
 should be able to adsorb and activate the reactants. Relevant in that respect
 are *inter alia* a sufficiently high pore volume, a sufficiently high specific
 surface area, a sufficient extent of dispersion of the catalytically active sites
 and a suitable acidity.

20 Suitable catalyst systems contribute to the following desired reactions
 1) to 5).

	Oxidation	1) NO + O ₂	→ NO ₂
		2) C _x H _y + O ₂	→ C _x H _y O _z or CO
25	H ₂ generation	3) C _x H _y + H ₂ O	→ H ₂ + CO + CO ₂
	NO _x reduction	4) NO/NO ₂ + C _x H _y /C _x H _y O _z /CO	→ N ₂ + CO ₂ + H ₂ O
	Hydrocarbon oxidation:	5) CH ₂ , C _x H _y O _z	→ CO ₂ and H ₂ O

The following undesired reactions 6) to 11) should be prevented as
 30 much as possible:

5	NOx conversion	6) NO ₂	→ NO + O ₂
		7) NO	→ N ₂ O
	Oxidation	8) NO ₂ + C _x H _y	→ CO, CO ₂ + NO
		9) SO ₂	→ SO ₃ (→ H ₂ SO ₄ with H ₂ O)
		10) C _x H _y	→ CO ₂
	Deposition	11) C _x H _y	→ C

As regards the selectivity, the catalyst system used should preferably promote the oxidation of hydrocarbons, without this leading to non-selective combustion. In other words, preferably, eventually reaction 4) is maximized, while reactions 6) to 11) are minimized. The catalyst system should also be stable to a sufficient extent at the temperature used, especially in the presence of components such as H₂O, SO₂, coke, Cl, As, P, Si. Also, the catalyst system used should offer sufficient resistance to mechanical erosion.

Very suitable catalyst systems that can meet the above-mentioned requirements are catalysts based on γ -Al₂O₃. γ -Al₂O₃ is active in CH₄-SCR, although according to the prior art this holds specifically at high temperatures. According to the invention, however, NO_x is for a considerable part present in the form of NO₂, which proves to be considerably more reactive than NO. γ -Al₂O₃ moreover offers a good sulfur and water tolerance and can easily be modified with different metals and additives.

Very suitable as catalyst support for CH₄-deNO_x under lean-burn conditions are *inter alia* different types of Al₂O₃, zeolites, in particular H-Zeolites (H-USY, H-FER, H-ZSM5, H-MOR), oxides such as ZrO₂, Ga₂O₃, perovskite and combinations (mixtures or layered structures) thereof. Perovskite is suitable in particular because it enables the simultaneous removal of NO_x and soot particles. As active phases on these supports, metals, metal ions and metal oxides can be used. Very suitable are silver

and platinum. Silver is specifically suited for reducing NO_2 . Platinum is suitable in particular because of the high activity at low temperatures. Other suitable metals are In, Ce, Au, Fe, Pd and Sn, because these are capable of reducing NO_2 very effectively. Finally, BaO-based systems are
5 mentioned. This so-called storage reduction catalyst can bind NO_x in the form of nitrates and in this way enhance the activity of the catalyst system.

A suitable catalyst system for plasma-assisted deNO_x in lean burn gas engines comprises, for instance, Ag/ Al_2O_3 or Ag/H-Zeolite. Such a system gives a high conversion, possesses a good stability and is especially active
10 for the conversion of NO_x with partially oxidized hydrocarbons (for instance MeOH). Other examples include In/Zeolite $\text{In}_2\text{O}_3/\text{Ga}_2\text{O}_3$, Pt/ Al_2O_3 , etc.

A suitable catalyst system for plasma-assisted methane oxidation in lean-burn gas engines comprises, for instance, Ag or Pt on Al_2O_3 or H-Zeolite support. However, also other catalysts that are proposed by others
15 as oxidation catalyst for hydrocarbons can be suitable.

For plasma-assisted deNO_x in stoichiometric engines, specifically all three-way catalysts are suitable, such as they have currently been developed by third parties, and are mostly based on rhodium, platinum or platinum on an alumina support, with sometimes additions of cerium,
20 lanthanum, zirconium or cerium.

In the embodiment schematically represented in Fig. 1A, the off-gas (1) to be cleaned is first passed through a plasma reactor, which is connected at (2) with a voltage source. Next, the gas stream passes the catalyst bed. The cleaned gas is obtained at (3).

25 The reference numerals in Fig. 1B have corresponding meanings to Fig. 1A. In this embodiment, plasma reactor and catalyst bed are integrated. This provides two advantages over the sequential embodiment of Fig. 1A: in the first place, a more compact plant is obtained. In the second place, any reverse reactions (for instance of the activated NO_2 to NO) are

prevented because the more active components can react away directly over the catalyst.